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Dynamics of GaAs photocarriers probed with pulsed infrared synchrotron radiation

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Abstract

Synchrotron radiation is a source of high brightness, pulsed infrared light that is well suited to the study of materials by pump-probe spectroscopy. A synchronized laser produces pump pulses and synchrotron infrared pulses serve as the probe. This method has been used for a number of time-resolved investigations, including a study of the frequency-dependent conductivity of photocarrier relaxation in GaAs. For this material, a Drude model gives a good description of the photoconductivity, but requires that the average carrier scattering rate change from electron like to hole like during the decay process (a few nanoseconds). This behavior suggests the rapid trapping of electrons, as may occur near a surface with defect states.

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1. Introduction

Synchrotron radiation serves as a pulsed infrared source that can be used for time resolved (pump probe) spectroscopy. The synchrotron pulses, which serves as the probe, usually determine the time resolution, with typical pulse lengths ranging from a few 10 s of picoseconds up to about 1 ns. Although laser sources achieve considerably shorter pulses, the synchrotron provides continuous spectral coverage and has proven very suitable for high-performance FTIR spectroscopy, including in the very far infrared. Future synchrotron radiation facilities have the potential for providing significantly shorter pulses (well under 1 ps), opening new areas of research. A detailed description of the use of synchrotron infrared pulses for time-resolved spectroscopy is published elsewhere [1].

A basic application of the pump-probe method is the study of photocarrier relaxation in semiconductors. The relaxation times vary considerably among materials and for a given material depend on defects within the bulk or at the surface. Lifetime values can range from a few picoseconds to greater than seconds. Spectroscopy is an attractive method for sensing photocarriers (as well as other excitations in a system) since the technique is non-contacting and can explore a wide range of energies. For example, measurements of the intraband (Drude) absorption in the far

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infrared ($\lambda > 100$ μm) can yield carrier densities and mobilities (or the electronic scattering time) [2]. This work describes a far-IR pump-probe spectroscopy study of photocarrier relaxation in semi-insulating (SI) GaAs.

2. Measurement

The study was performed using infrared beamline U4IR at the NSLS [3]. Probe pulses of ~1 ns duration and pulse repetition rate of 5.9 MHz were produced by operating the VUV ring with a single bunch of circulating electrons. A pulsed diode laser provided pump pulses of 1 ns duration and energy of about 1 nJ. The laser operated at a wavelength of 845 nm, or a photon energy of 1.47 eV, which is just sufficient for photoexciting GaAs (bandgap of 1.42 eV at $T = 300$ K). The total available photons per pulse was approximately 2×10^9.

The specimen was a semi-insulating GaAs wafer (100 orientation), approximately 0.5 mm thick. The pieces used in the study had been repeatedly handled and used for testing in other experiments, so the detailed pedigree was not known. Thus, some of the results may not be intrinsic to pristine GaAs. Both the laser and far-IR light illuminated the sample from the same side, through a 2 mm diameter circular aperture. Taking into account coupling and reflection losses, each laser pulse produced an estimated 2×10^{10} electron–hole pairs per cm^2.

Absorption by the photo-induced carriers is sensed as a transmission change. The conventional photo-induced transmission change is defined as $-\delta\mathscr{T}/\mathscr{T} \equiv -(\mathscr{T}' - \mathscr{T})/\mathscr{T}$ where $\mathscr{T}'$ and $\mathscr{T}$ are, respectively, the transmission measured with the laser source on and off. A time-dependent measurement can be similarly defined, with $\mathscr{T}'$ the transmission for a particular pump-to-probe delay time and $\mathscr{T}$ the transmission at some reference time. The natural choice for this reference time is the instant *before* a pump pulse is incident when the specimen is in its most relaxed state. For this situation the notation $-\delta\mathscr{T}(t)/\mathscr{T} \equiv -(\mathscr{T}(t) - \mathscr{T}_{\text{before}})/\mathscr{T}_{\text{before}}$ is used. Here, t is any pump-to-probe delay time of interest. Note that $|-\delta\mathscr{T}(t)/\mathscr{T}|$ is often largest at $t \approx 0$, i.e. the transmission change is largest between the moment just prior to a pump pulse and the moment at which a pump pulse is absorbed.

Next it is shown that a simple relationship exists between the photo-induced signal and the change in the material's optical conductivity. The absorption coefficient for GaAs is about 10^4 cm^{-1} so the photocarriers are produced in a thin layer about 1 μm thick [4]. In this situation one considers the transmission through a thin absorbing film (of thickness d) into a transparent substrate having refractive index n,

$$\mathscr{T} = \frac{4n}{(y_1 + n + 1)^2 + y_2^2}, \tag{1}$$

where $y = y_1 + \mathrm{i}y_2 = (4\pi/c)d(\sigma_1 + \mathrm{i}\sigma_2)$ is the dimensionless complex admittance of the thin conducting layer [5]. Note that this expression ignores multiple internal reflections within the substrate. In the limit of small conductivity (in particular $|y| \ll n$), the dependence on the imaginary part of the complex conductivity drops out and Eq. (1) simplifies to

$$\mathscr{T} \cong \frac{4n}{(n+1)^2}\left[1 - \frac{2y_1}{(n+1)}\right], \tag{2}$$

in which case the photo-induced transmission change becomes

$$\frac{-\delta\mathscr{T}}{\mathscr{T}} \cong \frac{2}{n+1}\delta y_1 = \frac{4\pi}{c}\frac{2\delta(\sigma_1 d)}{n+1}. \tag{3}$$

Comparing results from this expression with those from an exact calculation (that includes multiple internal reflections) shows that Eq. (3) is accurate to within 10% when $n \leqslant 4$ (most materials). With $n = 3.5$ for GaAs and noting that $4\pi/c = 377\ \Omega$ (the impedance of empty space), one arrives at the simple result,

$$\frac{-\delta\mathscr{T}}{\mathscr{T}} \cong 168\,\delta(\sigma_1 d), \tag{4}$$

where σ_1 is the induced frequency-dependent conductivity, measured in units of (ohm-cm)$^{-1}$ when d is in cm. Note that at zero frequency, $\sigma_1 d = \sigma_0 d = 1/R_\square$ where $R_\square$ is the so-called sheet resistance.

The real part of the complex conductivity for mobile charge carriers can be described by the Drude function,

$$\sigma_1(\omega) = \frac{\sigma_0}{1+(\omega\tau)^2} = n_c e\mu \frac{1}{1+(\omega\tau)^2} = \frac{n_c e^2 \tau}{m} \frac{1}{1+(\omega\tau)^2}, \quad (5)$$

where τ is the scattering rate for charge carriers of mass m and density n_c. This can be generalized to more than one type of charge carrier (e.g. electrons and holes) by using a Drude function for each. When electrons and holes are present in equal numbers, the electron contribution dominates due to the much greater mobility of the electrons ($\mu_e = 7000$ cm^2/V s) over the holes ($\mu_h = 400$ cm^2/V s) [6]. The scattering times τ_e and τ_h can be calculated from the mobility and effective masses ($m_e = 0.07m_0$; $m_h = 0.5m_0$). When ω is expressed in wavenumbers, the resulting Drude scattering rate (or width) $\Gamma = 1/2\pi c\tau$ is 16 cm^{-1} for the electrons and 47 cm^{-1} for the holes. Thus the Drude width may be used to discriminate between the two types of carriers for this material. This assumes that the material is of sufficiently purity and crystallinity that phonon scattering is dominant.

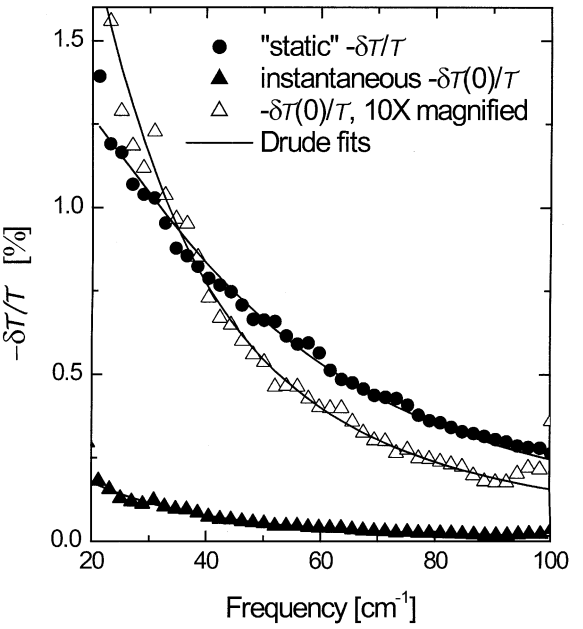

Fig. 1. Photo-induced far infrared transmission change $-\delta\mathscr{T}/\mathscr{T}$ for GaAs. Solid circles: static (slow response) photo-induced transmission change $-\delta\mathscr{T}/\mathscr{T}$. Solid triangles: measured $-\delta\mathscr{T}(0)/\mathscr{T}$, also shown magnified 10 times (open triangles) to illustrate the distinctly different Drude width when compared to the static $-\delta\mathscr{T}/\mathscr{T}$. Solid curves: Drude fits to both the static $-\delta\mathscr{T}/\mathscr{T}$ and $-\delta\mathscr{T}(0)/\mathscr{T}$.

3. Results and analysis

Initial measurements were performed without running the spectrometer, allowing the full range of wavelengths from 20 to 100 cm^{-1} through to the detector. Both conventional photo-induced (static $-\delta\mathscr{T}/\mathscr{T}$) and $-\delta\mathscr{T}(0)/\mathscr{T}$ signals were found, with the static signal approximately 10 times the largest time dependent signal. This indicates a decay component with relaxation time greater than the time interval between pulses (170 ns). Also, the magnitude of the static photo-induced signal was small (a few percent), confirming that the measurements were being performed in the weak perturbation limit and that the assumptions leading to Eq. (2) were valid. Measurements of $-\delta\mathscr{T}(t)/\mathscr{T}$ for t ranging from 0 ns out to 65 ns revealed a rapid initial decay component (less than 20 ns), followed by a slower decay. Thus the photoexcitations appear to relax according to a two-component decay with $\tau_{short} < 20$ ns and $\tau_{long} \gg 100$ ns. Signal-to-noise, which can be gauged from the scatter in the data, exceeded 10^4. The photo-induced spectra (both static and time resolved) were found to be in good agreement with a Drude conductivity, as shown in Fig. 1. Note that a single Drude function was used, as the available spectral range was not sufficient to yield unique fits to a conductivity function having both electron and hole terms. The fit results for the induced conductivity (per area) and scattering rate are shown in Figs. 2 and 3 as functions of time.

An interesting feature from the fits is the abrupt increase in scattering rate from 25 cm^{-1} to nearly 50 cm^{-1} during the first 10 ns following the photoexcitation pulse. These two values are comparable to the electron (16 cm^{-1}) and hole (47 cm^{-1}) scattering rates for GaAs, suggesting that electrons dominate at early times, but rapidly decay leaving

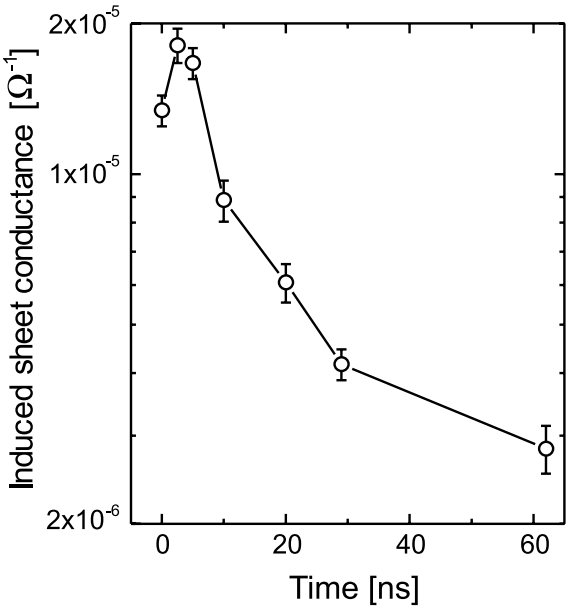

Fig. 2. Time-dependent photoconductance (per square area) extracted from Drude fits to $-\delta\mathscr{T}(t)/\mathscr{T}$ taken at various pump-probe delay times t. The values are relative to $t = 100$ ns.

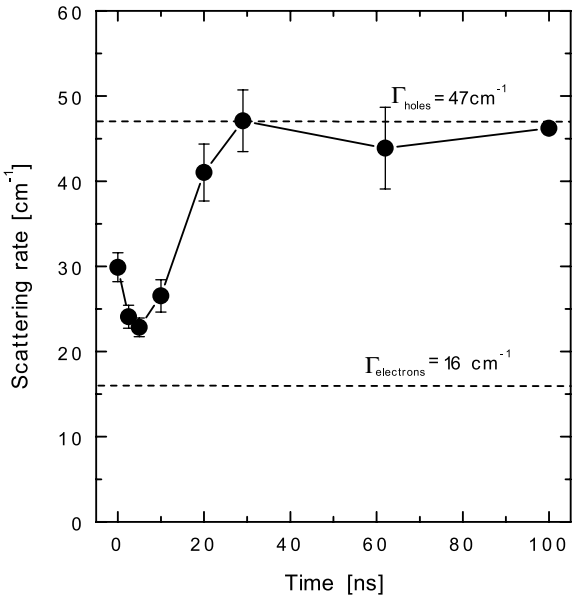

Fig. 3. Time-dependent scattering rate $\Gamma(t) = 1/(2\pi c\tau)$ from Drude fits to $-\delta\mathscr{T}(t)/\mathscr{T}$. The expected values of $\Gamma = 16$ cm^{-1} for electrons and $\Gamma = 47$ cm^{-1} for holes are also indicated.

a persistent hole contribution. Also, fits to the static $-\delta\mathscr{T}/\mathscr{T}$ spectra give the same hole-like scattering rate indicating that long decay component ($\gg$170 ns) is also due to holes. Using Eq. (4) and the measured value of $-\delta\mathscr{T}(0)/\mathscr{T}$, the photo-induced conductivity per pulse is determined to be 1.7×10^{-5} Ω^{-1}. Even though equal number of mobile electrons and holes are produced per pulse, $-\delta\mathscr{T}(0)/\mathscr{T}$ is dominated by the mobile electrons due to their smaller mass and scattering rate. Using $\sigma = n_c e\mu$. yields an induced electron density of 2.4×10^{10} cm^{-2} per pulse. This is in good agreement with the estimate determined from the incident photon fluence (2×10^{10} absorbed photons per cm^2). The fitted scattering rate of 25 cm^{-1} (as opposed to 16 cm^{-1}) suggests that the mobility μ_e is closer to 4500 cm^2/V s. This value is smaller than for pure, bulk material ($\mu_e = 7000$ cm^2/V s) as might be expected from surface or impurity scattering. Indeed, the electron mobility for S–I GaAs is often between 4000 and 5000 cm^2/V s when the purity is less than ideal [6]. Since the hole relaxation time appears to be much greater than the 170 ns between pulses, the measured hole concentration is essentially an equilibrium value where the average excitation and relaxation rates are equal. The equilibrium hole density can be determined from the static $-\delta\mathscr{T}/\mathscr{T}$ in the same manner as for the electrons (but with $\mu_h = 400$ cm^2/V s), yielding a value of 1.3×10^{12} cm^{-2}. Equating the generation rate (2×10^{10} cm^{-2} e–h pairs every 170 ns) and the relaxation rate ($1.3 \times 10^{12}/\tau_h$) yields an estimated $\tau_h = 11$ μs, three orders of magnitude longer than the electron decay time.

4. Discussion and summary

One plausible explanation for the large difference in electron (~10 ns) and hole (~10 μs) decay times involves surface states. For example, shallow defect states at the surface would normally act as donors, forcing the surface to be slightly n-type. Band-bending would then lead to an internal electric field pointing away from the surface. Such a field would cause the electron of a photogenerated e–h pair to be directed to the surface where it can quickly trap in one of the empty donor states,

ceasing to absorb as a mobile carrier. The same field directs the hole away from the surface, impeding its ability to recombine with an electron and resulting in an anomalously long hole lifetime.

This simple picture is valid as long as the photogenerated electron–hole surface density is lower than the surface state density. A higher density could significantly affect the occupation of the surface (trap) states and also screen the internal field. The number of trapped photoelectrons is not directly sensed in the measurement, but their density can be determined from the photo-induced hole density (since they must be equal). As noted above, the quasi-equilibrium concentration of holes is 1.4×10^{12} cm^{-2}, smaller than the $\sim 2 \times 10^{13}$ cm^{-2} value for the typical surface state density in GaAs as determined from photo-reflectance spectroscopy [7]. Therefore, the band-bending should be maintained at a more-or-less fixed level throughout the process.

An interesting test of this model would be to increase the photon fluence such that the photoelectron density exceeds the surface state density, saturating the traps and flattening the bands. Without the internal field to separate the charges, the hole recombination rate should increase. If observed, the technique could then be used as a contactless measure of the surface state density without the need for a specific sample or device architecture. Another test would make use of a tunable pump laser, allowing the penetration depth to be increased such that the surface plays a lesser role in the recombination process. It is hoped that such measurements can be performed in the near future.

In summary, pump probe far infrared spectroscopy has been successfully used to study the photoexcitation and recombination process in semi-insulating GaAs. The different scattering rates for electrons and holes allow them to be differentiated in far infrared absorption measurements. Time-resolved measurements show a rapid ($\sim$10 ns) decay of excess electrons and a much slower ($\sim$10 μs) decay of the associated holes. A model based on surface states and band bending is offered to explain this behavior. Further tests on well-characterized materials are needed for confirmation.

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